Quantum fluctuations in the cohesive force of metallic nanowires

C. Höppler* and W. Zwerger
Sektion Physik, Ludwig-Maximilians-Universität München, Theresienstraße 37, D-80333 München, Germany
(February 1, 2008)

Based on the recent free electron model for cohesion in narrow metallic constrictions by Stafford et al., we calculate the quantum fluctuations in the cohesive force versus elongation. The fluctuations are dominated by states near the Fermi energy, thus explaining their apparently universal magnitude of order ε_F/λ_F. We present numerical results for the force fluctuations in a simple geometry and show that they are well described by the contributions of a few classical periodic orbits in the Balian-Bloch trace formula for the density of states of transverse motion.

73.23.Ps, 03.65.Sq, 62.20.Fe

The mechanical properties of atomic size constrictions between two reservoirs of standard metals, for example Au, have been the subject of intensive research in the past few years.[1–3] In particular, simultaneous measurements of the cohesive force and the electrical conductance[4,5] have shown a striking correlation between the mechanical and transport properties. In a regime where the cohesive force is linear in the elongation ('elastic stage'), the electrical conductance exhibits plateaus similar to those found in two dimensional quantum point contacts in semiconductor heterostructures.[6,7] By contrast, both the conductance and the elastic force rapidly decrease in the narrow regime between two conductance plateaus ('yielding stage'). These observations were originally explained[4] in terms of abrupt atomic rearrangements which appear with increasing elongation and indeed classical molecular dynamics simulations[8–10] seem to support this point of view. On the other hand, the apparent similarity between the conductance plateaus found here and in semiconductor quantum point contacts together with the strong correlation between conductance and force suggests that elastic and yielding stages in the cohesive force may appear even for a smooth constriction geometry as a result of changing the number of discrete transverse modes for the electrons.[11]

This suggestion has recently been developed by Stafford, Baeriswyl, and Bürki.[12] It is based on viewing the transverse eigenstates of the conduction electrons as delocalised chemical bonds which provide both conduction *and* cohesion. Remarkably, a corresponding free electron model qualitatively accounts both for the average cohesive force and for the abrupt steps in the force of order ε_F/λ_F which are caused by successively cutting off the discrete electronic modes in the constriction. Now it is evident that any purely electronic model is an idealization of the true experimental situation. For instance, possible atomic rearrangements which reveal themselves through a hysteretic behavior of the force[4] are neglected. A realistic electronic description moreover has to account for the strong deviations from a naive conductance quantization picture arising from the rather small value of the Fermi wavelength which makes the electronic motion sensitive to defects even on an atomic scale.[13] Nevertheless, the simple free electron model of Stafford et al. not only provides an intuitive explanation of the observed behavior but also gives a correct order of magnitude estimate of the relevant forces, in the same way perhaps as the measured bulk modulus of many metals is roughly determined by the ground state Fermi gas pressure of the conduction electrons.[14]

In our present work we discuss the fluctuations in the cohesive force which arise from the discreteness of the electronic eigenstates for motion in the direction transverse to the elongation.[15] As shown by Stafford et al., the electronic cohesive force F of a constriction of length L is obtained from the $T = 0$ free electron grand canonical potential

$$\Omega = -\frac{8}{3}\frac{\varepsilon_F}{\lambda_F}\int_0^L \mathrm{d}z \int_0^{\varepsilon_F} \mathrm{d}E\, \rho_\perp(E,z)\left(1 - E/\varepsilon_F\right)^{3/2} \quad (1)$$

simply via $F = -\partial\Omega/\partial L$. Here $\rho_\perp(E,z)$ is the differential density of states (DOS) for the transverse motion of the electrons at a given cross section (z = const.). Within a semiclassical description, which is valid as long as the Fermi wavelength λ_F is much smaller than the constriction width R, the DOS may be split into an average $\bar{\rho}_\perp(E,z)$ and a fluctuating contribution $\delta\rho_\perp(E,z)$. The latter vanishes if averaged over an energy range much larger than the spacing $\Delta(z)$ between successive transverse eigenstates. Assuming the deformation occurs at constant total volume V, the average cohesive force $\bar{F}$ which is associated with the average DOS has only two contributions for $\lambda_F \ll R$:[12,16]

$$\bar{F} = -\frac{\varepsilon_F}{\lambda_F}\left[\frac{k_F}{8}\left.\frac{\partial S}{\partial L}\right|_V - \frac{4}{9}\right]. \quad (2)$$

Here the dominant contribution is associated with the (electronic contribution to the) surface tension, giving a cohesive force proportional to the change in surface area S with elongation L. In addition there is a universal

*Present address: Institut für Angewandte Physik, Eberhard-Karls-Universität Tübingen, Auf der Morgenstelle 10, D-72076 Tübingen, Germany.

contribution $\frac{4}{9}\frac{\varepsilon_F}{\lambda_F}$ to the average cohesive force which is completely independent of the geometry.[16] It arises from the topological term in the Weyl expansion for the integrated DOS[17] and leads to a weakening of the cohesion compared to the macroscopic surface tension contribution. As is evident from equation (2), the average cohesive force does not depend on the detailed geometry of the nanosize constriction which will presumably vary significantly between different realizations of an experiment. Regarding the force fluctuations δF which arise from the fluctuating part of the DOS, it was found in the numerical calculations[12] that the precise form of δF is specific to the shape of the cross section but does not depend on the detailed form of the constriction radius $R(z)$ versus z. Remarkably, the rms amplitude of these fluctuations turned out to have a universal magnitude

$$\mathrm{rms}(\delta F) \approx 0.3\frac{\varepsilon_F}{\lambda_F} \tag{3}$$

independent of geometry. In order to understand these observations, we note first that δF is determined by the fluctuations in the DOS of *transverse* motion. Following recent work[15,18,19] we may therefore assume a simple cylindrical form $R(z) = \text{const.}$ for the constriction with a radius R which scales like $L^{-1/2}$ in order to fulfill the constraint of constant volume. Since the discrete eigenenergies ε_ν for transverse motion all scale like R^{-2}, we have $\partial\varepsilon_\nu/\partial L = \varepsilon_\nu/L$. It is then easy to show from (1) that in this simple geometry the fluctuations of the cohesive force at fixed total volume are given by

$$\delta F|_V = \frac{8}{3}\frac{\varepsilon_F}{\lambda_F}\int_0^{\varepsilon_F} \mathrm{d}E\,\delta\rho_\perp(E)\left(1-\frac{5}{2}\frac{E}{\varepsilon_F}\right)\left(1-\frac{E}{\varepsilon_F}\right)^{1/2}. \tag{4}$$

Here $\delta\rho_\perp(E)$ is the fluctuating transverse DOS at the narrowest point of the constriction, which also determines its conductance G. Now, in contrast to G which is a property of the states directly *at* the Fermi energy, the cohesive force obviously depends on *all* the states with energies between zero and ε_F. The numerical calculations[12,19], however, which show that the force oscillations are directly correlated with the conductance, indicate that δF is dominated by the states near the Fermi energy. Indeed, this observation can be understood easily from equation (4), at least on a qualitative level. Since the fluctuating DOS $\delta\rho_\perp(E)$ is a rapidly oscillating function which varies on a scale of the order of the mean level spacing $\Delta \ll \varepsilon_F$, the contributions to $\delta F|_V$ in (4) from energies between zero and close to ε_F cancel. It is only in a small range of several level spacings near the upper integration limit, where the factor $(1-E/\varepsilon_F)^{1/2}$ changes rapidly on a scale on which the DOS varies. Therefore only the contribution to δF from a few states below the Fermi energy survives in (4). As a result, $\mathrm{rms}(\delta F)$ is expected to be of order ε_F/λ_F independent of the constriction radius R, a property which has been verified numerically up to values $k_F R = 200$ by Stafford et al.[12,20] By contrast, if all the states from zero up to ε_F were to contribute to the force fluctuations, δF would scale as the fluctuations in the *total* number of states $N(\varepsilon_F)$ below the Fermi energy. Assuming Poisson statistics, appropriate for a classically integrable transverse motion[21], one has $\mathrm{rms}N(\varepsilon_F) = \bar{N}^{1/2}(\varepsilon_F) \sim k_F R$. The force fluctuations would thus increase with the constriction radius, in contradiction with the results of Stafford et al.[12]

For a quantitative confirmation of our arguments above, we have calculated numerically the force fluctuations which follow from (4) for a cylindrical constriction with radius $R(L) = R_0\sqrt{L_0/L}$. The corresponding results for δF in units of the fundamental force $\varepsilon_F/\lambda_F \approx 1\,\mathrm{nN}$ are shown in Fig. 1 for a wire which is stretched from $k_F R = 30$ down to $k_F R = 2$. Clearly, the force fluctuations are independent of $k_F R$, with an average magnitude $\mathrm{rms}(\delta F) = 0.6\,\varepsilon_F/\lambda_F$ which is of the same order as the topological contribution to the force (2).[22] The apparently complicated dependence of the force fluctuations on the elongation can in fact be simply understood as arising from only a few classical periodic orbits of electrons in the assumed circular cross section of the wire. Indeed, as is well known, the fluctuations in the DOS around its average value can generally be represented in terms of a sum over classical periodic orbits in a semiclassical approximation. For integrable systems such a connection between the quantum mechanical DOS and classical mechanics was first found by Balian and Bloch.[23] Specifically, for a circle the periodic orbits are regular polygons. They may be characterized by their number of vertices v and their winding number w. Obviously we have $v \geq 2w$. If there is a common divisor n between v and w, the orbit is an n-fold repetition of a primitive periodic orbit (see Fig. 2 for some elementary examples). Introducing an angle $\phi_{vw} = \pi w/v$, the length of a periodic orbit is $L_{vw} = 2vR\sin\phi_{vw}$ from simple geometry. The oscillating contribution to the DOS of a circular billiard can then be represented as[24]

$$\delta\rho_\perp^{sc}(E) = \frac{2}{\Delta}(\pi k_E R)^{-1/2}\sum_{w=1}^{\infty}\sum_{v=2w}^{\infty} f_{vw}\frac{\sin^{3/2}\phi_{vw}}{\sqrt{v}} \times \sin\left(k_E L_{vw} - 3v\frac{\pi}{2} + 3\frac{\pi}{4}\right). \tag{5}$$

Here $\Delta = \frac{\hbar^2}{mR^2}$ is the unit of energy and $f_{vw} = 1$ for $v = 2w$ or $f_{vw} = 2$ for $v > 2w$ the number of different periodic orbits through an arbitrary point within the circle. Using the semiclassical approximation (5) in our expression (4) for the force oscillations, we find that the details of the exact numerical result for δF are essentially explained by including only the three simplest periodic orbits $v = 2,\ 3,\ 4,\ w = 1$ in the circle (see Fig. 1). Extending the series to all the 16 orbits with $v \leq 10$ and $w \leq 2$, the agreement between the semiclassical and fully quantum mechanical calculation becomes essentially exact. The fact that only a few periodic orbits are required

to describe the force oscillations is a consequence of the integration over all energies in (4), which suppresses the DOS fluctuations on very short scales associated with longer periodic orbits.

Finally, it is interesting to point out that the approximation of simply adding the Weyl and trace formula contribution to the DOS, which apparently works very well for our present problem, is not always valid as has been shown very recently by Bhaduri et al.[25]

In conclusion, we have studied the quantum fluctuations in the cohesive force of metallic nanowires which arise from the discreteness of the electronic motion in the transverse direction. It has been shown that only a few states below the Fermi energy contribute to these fluctuations, supporting the prediction of universal force fluctuations $\mathrm{rms}(\delta F) = \mathrm{const.}\cdot\varepsilon_F/\lambda_F$ first found by Stafford et al.[12] Unfortunately even in our simple geometry we have not found an analytical derivation of this result. Indeed, in our semiclassical approach, if we substitute equation (5) into (4) and then change the integration variable to E/Δ it is not evident that the fluctuations are independent of $k_F R$. Therefore the issue of force fluctuations and in particular their geometry dependence deserves further investigation. The detailed structure of the force fluctuations reflects the classical periodic orbits in a given cross section which we have assumed to be circular here. It would clearly be of interest to generalize our results to the case of chaotic motion in the transverse direction where the eigenvalues obey random matrix theory rather than Poisson statistics. Similarly to the situation of persistent currents in ballistic billiard structures, we expect that the force fluctuations will be *smaller* if the transverse motion is chaotic.[26] Experimentally, the observation of the quantum fluctuations in the cohesive force as well as the closely related charge fluctuations of order e predicted very recently by Kassubek et al.[19] would constitute a crucial test of the electronic model of cohesion in metallic nanowires as opposed to a classical mechanical model.

We acknowledge David A. Wharam for carefully reading the manuscript.

[1] N. Agraït, G. Rubio, and S. Vieira, Phys. Rev. Lett. **74**, 3995 (1995).
[2] J. M. Krans et al., Nature **357**, 767 (1995).
[3] L. Olesen et al., Phys. Rev. Lett. **72**, 2251 (1994).
[4] G. Rubio, N. Agraït and S. Vieira, Phys. Rev. Lett. **76**, 2302 (1996).
[5] A. Stalder and U. Dürig, Appl. Phys. Lett. **68**, 637 (1996).
[6] B. J. van Wees et al., Phys. Rev. Lett. **60**, 848 (1988).
[7] D. A. Wharam et al., J. Phys. C **21**, L209 (1988).
[8] U. Landmann et al., Phys. Rev. Lett. **77**, 1362 (1996).
[9] T. N. Todorov and A. P. Sutton, Phys. Rev. Lett. **70**, 2138 (1993), Phys. Rev. B **54**, R14234 (1996).
[10] M. R. Sørenson, M. Brandbyge, and K. W. Jacobsen, Phys. Rev. B **54**, 3283 (1998).
[11] In fact, recent density functional calculations by H. Häkkinen and M. Manninen, Europhys. Lett. **44**, 80 (1998) indicate that changes in the number of transverse electronic modes may entail atomic rearrangements.
[12] C. A. Stafford, D. Baeriswyl and J. Bürki, Phys. Rev. Lett. **79**, 2863 (1997).
[13] E. Scheer et al., Phys. Rev. Lett. **78**, 3535 (1997) and Superlattices and Microstructures **23**, 747 (1998).
[14] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976), chapter 2.
[15] S. Blom et al., Phys. Rev. B **57**, 8830 (1998).
[16] C. Höppler and W. Zwerger, Phys. Rev. Lett. **80**, 1792 (1998).
[17] M. Kac, Am. Math. Monthly **73**, 1 (1966), for a recent discussion see e. g. G. Guiterrez and J. M. Yanez, Am. J. Phys. **65**, 739 (1997).
[18] J. M. van Ruitenbeek et al., Phys. Rev. B **56**, 12566 (1997).
[19] F. Kassubek, C. A. Stafford and H. Grabert, cond-mat/9809318 (1998).
[20] Note that their dimensionless Sharvin conductance $G_S = \frac{h}{2e^2} G$ is just equal to the average number $\bar{N}_\perp(\varepsilon_F)$ of transverse states at the narrowest point below the Fermi energy, which is $(k_F R/2)^2$ to leading order ($k_F R \gg 1$) for a circular cross section, see ref. 17.
[21] See e. g. F. Haake, *Quantum Signatures of Chaos* (Springer, Berlin, 1991).
[22] The rms of the force fluctuations is larger in this model than in that of Stafford et al.—cf. equ. (3)—because the smooth constriction geometry they considered leads to a rounding off of the peaks of the force fluctuations.
[23] R. Balian and C. Bloch, Ann. Phys. **69**, 76 (1972).
[24] S. M. Reimann et al., Phys. Rev. A **53**, 39 (1996), see also M. Brack and R. K. Bhaduri, *Semiclassical Physics* (Addison Wesley, Reading, Massachusetts, 1997), chapter 6.
[25] K. H. Bhaduri et al., chao-dyn/9803015 v2 (1998).
[26] F. v. Oppen and E. K. Riedel, Phys. Rev. B **48**, 9170 (1993).

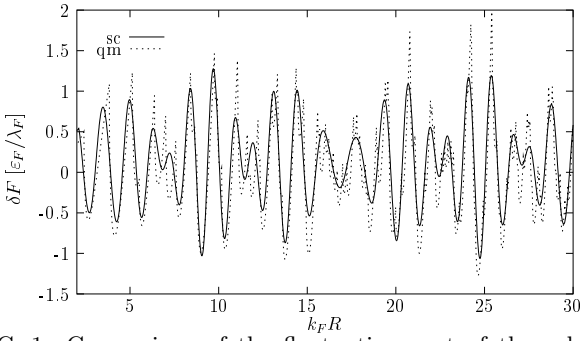

FIG. 1. Comparison of the fluctuating part of the cohesive force δF with δF^{sc}, calculated with three periodic orbits ($v = 2, 3, 4$, $w = 1$).

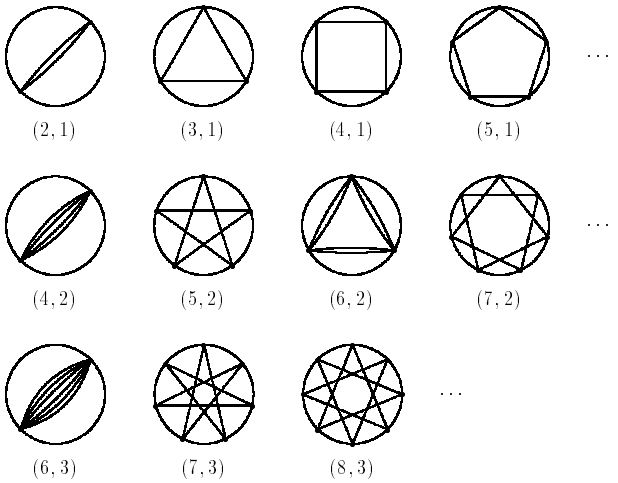

FIG. 2. Closed classical periodic orbits in a circlular billiard with reflecting walls. Between consecutive reflections the trajectory follows straight lines. The winding number w and the number of vertices v of the particular orbits are given as tupel (v, w) (after Balian and Bloch[23]).